APPENDIX M MONITORED NATURAL ATTENUATION

M.1 INTRODUCTION

M.1.1. What is Natural Attenuation

Natural attenuation occurs to some degree for any contaminant at any site as a result of physical, biological and chemical processes. Although natural attenuation occurs universally, it is not an appropriate method of addressing contaminant reduction at all sites. The decision to use natural attenuation as a remedial method must include an evaluation of the nature of the contaminant source and chemistry, and risk to human health and the environment.

Physical processes

Physical processes contributing to natural attenuation include dilution, volatilization and adsorption. Dilution may occur as a result of mechanical dispersion, diffusion and recharge. For recalcitrant contaminants, dilution is the main mechanism for natural attenuation.

Biological processes

Aerobic and anaerobic biological processes are the most important processes for natural attenuation, since they are the only natural mechanisms that result in an actual decomposition in contaminant mass.

Aerobic degradation is the process by which microbes in the presence of sufficient oxygen (>1 to 2 mg/l) metabolize organic contaminants. BTEX constituents of petroleum contamination can be *mineralized* by aerobic microbes by reducing the organic contaminant to inorganic constituents (*i.e.*, carbon dioxide and water). The oxygen in the presence of the microbes acts as an electron acceptor, thereby oxidizing the organic contaminant. The energy released by this process is used by the microbes for cell maintenance and growth.

Anaerobic degradation is the process by which microbes in the absence of sufficient oxygen metabolize organic contaminants. As aerobic degradation of contaminants proceeds, oxygen is depleted. If the rate of depletion of oxygen exceeds the rate of replenishment, the groundwater becomes hypoxic (0.1 to 2 mg/l) or anoxic, and is no longer able to support aerobic activities. When this occurs, degradation continues using alternative electron acceptors. Nitrate, manganese (IV), iron (III), sulfate and carbon dioxide are anaerobic electron acceptors. Anaerobic degradation is accomplished by a variety of anaerobic and facultative (able to switch from aerobic to anaerobic metabolism) microbes. Toluene and ethyl benzene readily degrade in anaerobic systems. Benzene and xylenes degrade with more difficulty. The anaerobic metabolism of benzene requires the efforts of multiple organisms to be complete.

Chemical processes

Chemical processes within the scope of this guidance include hydrolysis and dehydrohalogenation, which effect the halogenated compounds, *e.g.*, ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA).

M.1.2 Is MNA Appropriate for a LUST Site

Natural attenuation should not be a presumptive or default remedy, since passive treatment may allow preventable impact to human health or the environment to occur. Monitored natural attenuation (MNA) is not a “No further action” situation, since, as the name implies, the processes occurring are periodically being monitored.

Figure M.1.2.a is a simplified logic process for the evaluation of the appropriateness of MNA as a remedial alternative, alone or in combination with other remedial technologies, at a site once site characterization has been completed (see Section 7.3 for further details on development and evaluation of remedial alternatives in a CAP). The top portion of the flowchart deals with source factors and the bottom portion deals with risk factors. When using this flowchart for an initial evaluation of MNA, it may become apparent that data is lacking to support one or more steps in the flowchart. It is reasonable to proceed through the flowchart making reasonable assumptions regarding such matters as groundwater travel time, but if values become critical factors in the decision process, site-specific data should be gathered and evaluated before a CAP is submitted. This flowchart does not include the cost of implementing MNA as a factor in determining the appropriateness of MNA at a site, since this criteria is considered within the context of evaluating remedial alternatives in a CAP. In this flowchart, receptors are intended to include not only production wells, but those individuals exposed or potentially exposed to groundwater.

When free product is present and has been removed to the extent practicable, the department considers MNA to be a potential remedial alternative only when the natural attenuation process proceeds at a rate which is greater than or equal to the rate at which COCs in the non-aqueous phase flux into the aqueous phase. This results in a net mass balance of the COCs within the contaminant plume. Some indicators which suggest that the rate of dissolved phase influx exceeds dissolved phase reduction are plume migration, microbial “dead” zones due to toxicity, and increases in COC concentrations at a down-gradient or cross-gradient monitor well.

In accordance with A.R.S. § 49-1005(E), a LUST site may be closed when MNA is the selected remedial corrective action and attainment of the AWQS has not been achieved at the time of LUST site closure. This condition is solely dependent upon the adequate demonstration that MNA will achieve the AWQS during the time period established in the CAP, and that legal and administrative mechanisms are in place for the restriction of groundwater use in the interim period such that public health and the environment is protected until the AWQS is attained. Depending upon site conditions, off-site uses of groundwater, and potential off-site receptors, adequate COC reduction by MNA alone may not be achieved in the necessary time period and thus requires additional consideration of other remediation technologies to be used in concert with MNA.

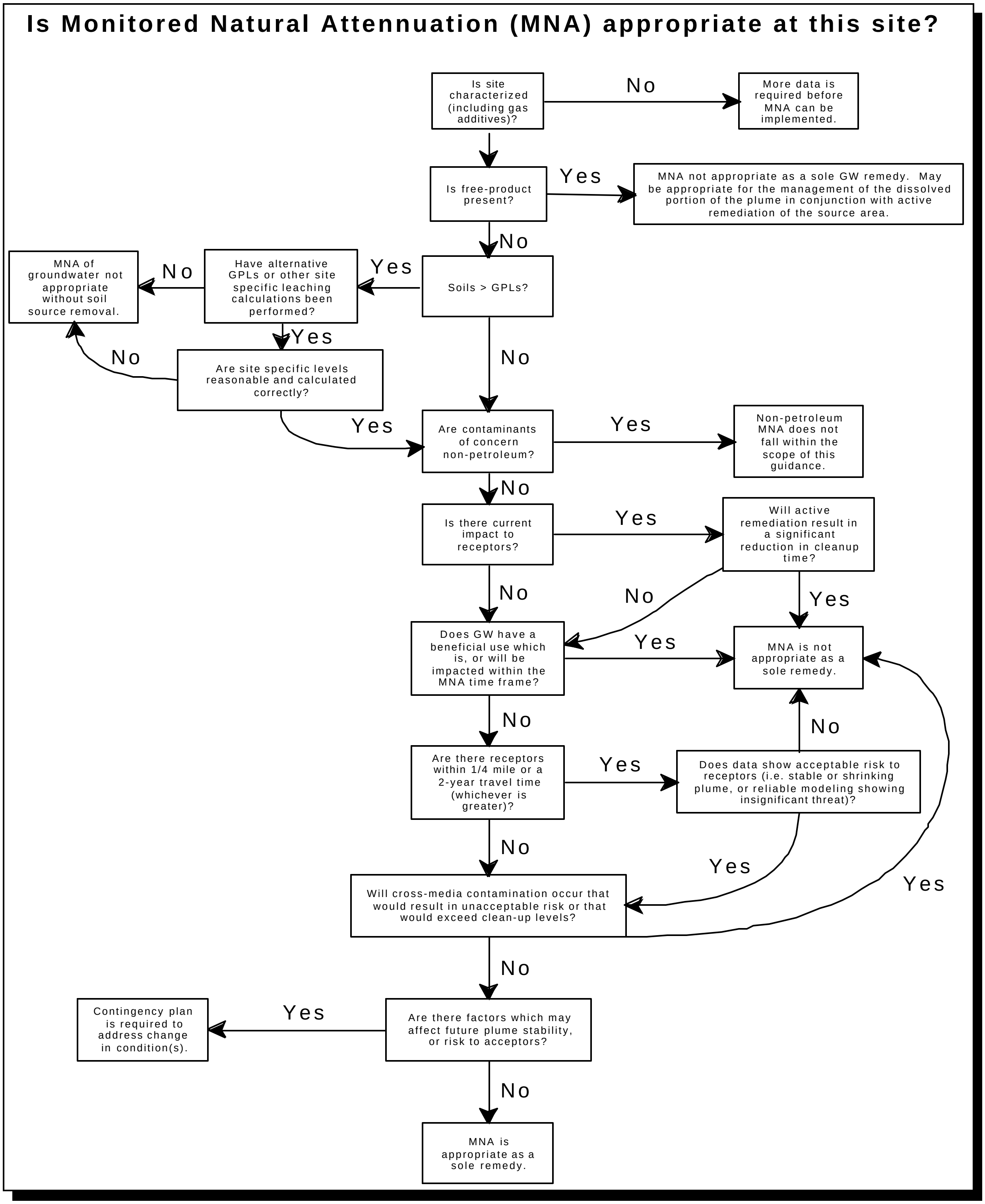

Table M.1.2.a MNA Flowchart for Use Evaluation

M.2 INVESTIGATION REQUIREMENTS FOR DEMONSTRATING NATURAL ATTENUATION OCCURRENCE AND APPLICABILITY

In order for MNA to be considered as a potential remediation technology for a site which may be used alone or in conjunction with other technologies, it must be demonstrated that natural attenuation is occurring and is applicable at the site in reducing contaminant concentrations. The appropriateness of MNA use at a site is dependent upon the time frame and costs associated with achieving the corrective action standards relative to other remedial alternatives evaluated in the CAP. As such, MNA is applicable at a site when the process of natural attenuation is occurring, and:

- The total extent of contamination has been determined and documented within a site characterization report.

- To the extent practicable, free product should be removed. This limits the the most significant contribution to additional dissolved phase contamination of the aquifer.

Natural attenuation is demonstrated to occur when hydrologic conditions have been established and one or more lines of evidence (see section M.3 for further discussion), as appropriate, have been determined at a site. Lines of evidence include contaminant plume status, rate of biodegradation, microbial and assimilative capacity. The investigative approach for determining the occurrence of natural attenuation requires the following minimum elements:

- An up-gradient well to establish the quality of groundwater entering the LUST site, the concentration of regulated substances, and, baseline conditions.
- A source well to establish the concentration of regulated substances at the point of release.
- Additional wells within the plume along the apparent centerline and the lateral edge of the plume to establish the status of the plume as stable, shrinking or expanding, and, when appropriate, the presence and levels of terminal electron acceptors and reduction products.
- A down-gradient well to establish the maximum extent of the groundwater plume in the direction of groundwater flow.
- A monitoring plan. The frequency of monitoring should be consistent with site-specific seasonal or event influencing water-level fluctuations, changes in contaminant concentrations, and hydraulic gradients. This frequency is typically established at four quarterly events over a one year period, but may vary with site-specific hydrologic conditions. Samples collected should be analyzed for

COCs and, if and when appropriate, geochemical parameters as discussed in section M.3.

M.3 LINES OF EVIDENCE FOR NATURAL ATTENUATION

The National Research Council (1993) and ASTM Standard E 1943-98 both suggest a similar approach of using three lines of evidence to demonstrate that natural attenuation is occurring. These lines of evidence should be used appropriately when presenting information regarding (a) the appropriateness of MNA as a remediation technology to be selected among remedial alternatives in a CAP, and (b) the progress of MNA in achieving the corrective action standard once implemented at a site. The following is a description of these lines of evidence.

M.3.1 Primary

The primary lines of evidence involve an evaluation of the concentrations of COCs determined by laboratory analyses of samples collected at monitor well locations over a suitable period of time to determine if the groundwater plume is shrinking, stable or expanding. The COC concentration data collected over time may then be plotted to establish trends in COC changes. This may be achieved using (a) overlays of plume contour maps from each monitoring event, (b) semi-logarithmic graphs of concentrations from individual wells versus time, and (c) a semi-logarithmic graph of the concentration versus the distance downgradient for a series of centerline wells in the direction of the flowpath from each monitoring event.

<u>Shrinking plume</u>: Evidence of natural attenuation because the natural attenuation rate exceeds the mass loading rate of chemicals of concern to groundwater.

<u>Stable plume</u>: Evidence of natural attenuation because the natural attenuation rate equals the mass loading rate of chemicals of concern to groundwater.

<u>Expanding plume</u>: No evidence of natural attenuation because the mass loading rate of chemicals of concern to groundwater exceeds the natural attenuation rate.

M.3.2 Secondary

The secondary lines of evidence involve the estimation of the attenuation rate and/or an evaluation of geochemical indicator data to determine if natural biodegradation is occurring.

The attenuation rate can be estimated using either a mass balance or a graphical/regression technique. The mass balance approach calculates the chemical of concern source rate (mass loading to groundwater) and is dependent on whether the plume is shrinking, stable or expanding. For example, the mass loading rate is approximately equivalent to the natural attenuation rate in the case of a stable plume. The graphical/regression techniques use the same data from the primary lines of evidence for concentration of chemical of concern plotted against time and/or distance from source. The slope of the straight line on a plot of log of the concentration versus time is the point attenuation rate. The slope of the straight line on a plot of the log of the concentration versus distance yields the bulk attenuation rate when multiplied by the average groundwater velocity.

Because the natural attenuation rate includes the rates of processes other than biodegradation, *i.e.*, dispersion, sorption, dilution, volatilization, advection, geochemical indicators may be used to demonstrate the potential for biodegradation in groundwater. The collection of the following geochemical data reflects the state of those metabolic steps in the reduction of organic molecules for energy and biomass production: dissolved oxygen (aerobic electron acceptor); nitrate (facultative anaerobic electron acceptor); sulfate (anaerobic electron acceptor), manganese (Mn^{+2}, reduced form of anaerobic electron acceptor Mn^{+4}), ferrous iron (Fe^{+2}, reduced form of anaerobic electron acceptor Fe^{+3}); methane (refractory anaerobic product); and redox potential (reflects the relative incidence of biological activity).

The following generally reflects the relationship between levels of BTEX and indicator concentrations within a plume. Of the indicators noted, only oxygen is a measured parameter of aerobic biodegradation:

BTEX	Oxygen	Nitrate	Mn(II)	Fe(II)	Sulfate	Methane
HIGH	LOW	LOW	HIGH	HIGH	LOW	HIGH
LOW	HIGH	HIGH	LOW	LOW	HIGH	LOW

It should be noted that it is the reduced form of manganese and iron which is measured in the field or laboratory which, when elevated, indicates that anaerobic activity is reducing the oxidized forms. It is not recommended that the refractory reduction product of carbon dioxide be measured due to the bicarbonate buffering capacity of the aquifer formation. Unless all significant contributions to alkalinity are known, it is typically not effective to measure these parameters in order to quantify the carbon dioxide produced. Methods for measuring the geochemical indicators discussed above are presented in the references listed in section M.5. It is recommended that those indicators which become unstable during the period of sampling collection and handling be assayed as soon as possible using field methodologies.

Typically, geochemical data may be presented as maps showing their distribution, or graphed as concentration versus distance or BTEX concentration.

M.3.3 Tertiary

The tertiary lines of evidence include solute transport modeling, estimates of assimilative capacity, and microbiological studies. Development of these lines of evidence typically require modeling which rely on further data collection for model input and calibration. The following is a description of additional lines of evidence for natural attenuation.

<u>Solute transport modeling</u>
There are a variety of models that can be used which include steady-state solutions and one-, two- and three-dimensional analytical solutions.

<u>Assimilative capacity estimates</u>
Through the use of indicator parameters, the potential mass of chemicals of concern degraded per unit volume by aerobic and anaerobic respiration can be estimated. The qualitative estimate determines the assimilative capacity of the measured electron acceptors to completely metabolize the chemical of concerns in groundwater.

<u>Microbiological studies</u>
This involves the use of laboratory assays documenting that microorganisms found in site-specific samples have the potential to transform the chemicals of concern under site-specific conditions. The laboratory assays can include either microbial counts or microcosm studies, *e.g.*, heterotrophs and petroleum degraders. Microbial populations may also be associated with levels of

macronutrients available in the aquifer formation, *i.e.*, nitrogen and phosphorus measured as ammonium, Kjeldahl nitrogen, phosphate, *etc*.

M.4 EVALUATING THE APPROPRIATENESS OF MNA

For LUST sites which have sufficient historical monitoring data, the primary lines of evidence (shrinking or stable plumes) may be adequate to demonstrate remediation of the contamination by natural attenuation.

For LUST sites which do not have sufficient historical monitoring data or if the primary lines of evidence is inadequate or inconclusive, the collection and evaluation of secondary lines of evidence can be adequate to demonstrate remediation of the contamination by natural attenuation. This may be the case for LUST sites where there has only been one or two groundwater monitoring events.

Additional lines of evidence may be useful for the small percentage of LUST sites where the primary and secondary lines of evidence are inconclusive to demonstrate remediation of the contamination by natural attenuation. Naturally occurring biodegradation of petroleum hydrocarbons is rarely limited by the availability of bacteria. Therefore, microbiological studies (microbial counts or microcosm studies) are not typically performed at petroleum release sites.

Applicability of MNA for use at a site becomes dependent upon the conceptual site model (CSM) which identifies the potential receptors which may be impacted, and the current and potential future uses of water resources and the health risks associated with these uses. In order to evaluate such potential health risks, the time of impact and levels of COCs at the point of exposure must be predicted for the MNA processes. These may be predicted using primary lines of evidence for on-site stable or shrinking plumes, or by using secondary lines of evidence for off-site plumes. Unacceptable levels of health risk estimated for potential future exposures may require that other technologies be applied in combination with MNA, or that MNA may not be applicable due to current off-site conditions or changes in on- or off-site conditions. When MNA is applicable for use at a site, alone or in combination with other remediation technologies, the CAP should also present information regarding the relative cost-effectiveness of this remediation alternative.

M.5 REFERENCES

American Petroleum Institute, 1998, Evaluation of Sampling and Analytical Methods for Measuring Indicators of Intrinsic Bioremediation, API Soil and Groundwater Research Bulletin, No. 5.

American Society for Testing and Materials, ASTM Standard E 1943-98, Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites.

U.S. Environmental Protection Agency, 1999, Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, OSWER Directive 9200.4-17P.

Air Force Center for Environmental Excellence (AFCEE), 2000. Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation.